Syo Kurokawa\*, J.A. Elix\*\*, P.L. Watson\*\* & M.V. Sargent\*\*\*:

\*\*Parmelia notata, a new lichen species producing two new depsidones

黒川 逍\*・J. A. エリックス\*\*・P. L. ワトソン\*\*・M. V. サージェント\*\*\*: 二種の新しいデプシドンを含むウメノキゴケ属の新輝

# (Plates I-II)

In this paper, an Australian lichen, *Parmelia notata*, is described as new to science. Two new depsidones, 4-O-methylhypoprotocetraric acid [1'-carboxy-2'-hydroxy-4-methoxy-3, 3', 6, 6'-tetramethyl-depsidone (I)] (Culberson 1966) and notatic acid [1'-carboxy-2'-hydroxy-4-methoxy-3, 6, 6'-trimethyl-depsidone (II)] (Culberson 1966) have been isolated from the species and characterized.

Fig. 1. The structures of two new depsidones. (I): 4-0-methylhypoprotocetraric acid. (II): notatic acid.

#### Taxonomic Notes

Parmelia notata Kurokawa, sp. nov.

Thallus ad saxa adnatus vel laxe adnatus, sulphureo-lutescens, di- vel trichotome lobatus, 6-14 cm diametro; lobi sublineariter elongati, saepe imbricati, plurimum apicem versus plus minusve ascendentes, ciliis destituti, 0.7-2.0 mm lati,  $240-280 \,\mu$  crassi. Superficies superior albo-notata vel effigurato-maculata, saepe fusco- vel nigro-marginata, isidiis sorediisque desti-

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tuta; medulla alba; superficies inferior nigra, plus minusve rugulosa, rhizinata, rhizinis nigris, maxime sparsis, simplicibus, validis, 0.5-1.2 mm longis. Cortex superior prosoplectenchymatus, irregulariter incrassatus,  $25-85~\mu$  crassus; stratum gonidiale continuum,  $27-48~\mu$  crassum; stratum medullare ca.  $130~\mu$  crassum, cortex inferior fuscus vel fusco-niger,  $20-25~\mu$  crassus.

Apothecia sessilia, 4-10 mm diametro, disco fusco, saepe radiatim fisso, amphithecio effigurato-maculato; hymenium hyalinum, ca. 50  $\mu$  altum; asci subclavati, 8-spori, sporis ellipsoideis, simplicibus, hyalinis, 3-4×6-8  $\mu$ .

Superficies superior K+plus minusve lutescens, KC+lutescens; medulla K-, P-, C-, KC-; thallus acidum usnicum, acidum 4-O-methylhypoprotocetraricum, et acidum notaticum continens.

Type specimen. On rock, sandstone escarpment on the road 5 miles east of Nerriga, New South Wales, Australia, elevation about 750 m. S. Kurokawa 6401—holotype in TNS and isotype in MEL.

The present new species (Pl. I, fig. 1) belongs to the subgenus Xanthoparmelia and is characterized by having effigurate maculae on the upper surface of lobes (Pl. I, fig. 2) and by producing two new depsidones, 4-O-methylhypoprotocetraric and notatic acids, along with usnic acid. It may be related to Parmelia hypoleia Nyl., an African species of Xanthoparmelia, which also has effigurate maculae on the upper surface of lobes. It is, however, clearly distinguished from P. hypoleia by colour reaction of the medulla with P (1% alcohol solution of p-phenylendiamine); the medulla is P— in P. notata whereas it is P+ orange red in P. hypoleia as it contains protocetraric acid. Thalli of P. notata, in addition, are adnate to loosely adnate and the lobes are 0.7-2.0 mm wide, while those of P. hypoleia are a little more loosely adnate and the lobes are 0.5-1.0 mm wide, being more or less narrow-lobulate.

This new species seems to be rather common in eastern New South Wales, Australia, including the Australian Capital Territory, with range extension southward to Tasmania and westward to Western Australia.

Additional specimens examined. AUSTRALIA: New South Wales. Moonbi Lookout, Moonbi Ranges, Main Divide, 17 miles north of Tamworth, elevation about 800 m. S. Kurokawa 5155 (TNS) and 5159 (H, TNS). On rock surfaces, near Coppin's Crossing, A. C. T. J. A. Elix (TNS). Sandstone escarpment on the road 5 miles east of Nerriga, elevation about 750 m. S.

Kurokawa 6400 (TNS) and 6402 (DUKE, TNS). Western Australia. Snake Rocks, 28 miles south-east of Perth, elevation about 270 m. S. Kurokawa 6637 (PERTH, TNS). Tasmania. Van Diemens Land. Ch. Stuart 1133 (MEL, 6179).

## Chemical Notes

Macrochemistry. The thalli of *P. notata* Kurok. (100 g) were extracted continuously with ether (24 hr) and the extract evaporated to dryness to give a yellowish solid. This solid was extracted with hot benzene (50 ml) and the extract diluted with ethanol (100 ml) to subsequently yield usnic acid (0.66 g, 0.7%). The remaining solid was then recrystallized several times from dimethylformamide to yield 4-O-methylhypoprotocetraric acid (3.0 g, 3%) as colourless needles, m. p. 228-229° dec.<sup>1)</sup> (Found: C, 63.7; H, 5.1%, C<sub>19</sub>H<sub>18</sub>O<sub>7</sub> requires C, 63.7; H, 5.1). This compound gave a blue-violet colouration with alcoholic ferric chloride solution and exhibited the expected spectral characteristics. The dimethylformamide mother liquors were diluted with water and extracted with benzene. The benzene extract was washed with water, concentrated, and the residue recrystallized from acetone to give notatic acid (2.1 g, 2.1%) as colourless needles, m. p. 225-226° dec.<sup>1)</sup> (Found: C, 63.1; H, 4.8. C<sub>18</sub>H<sub>16</sub>O<sub>7</sub> requires C, 62.8; H, 4.7%). This compound gave a distinct purple colouration with alcoholic ferric chloride solution.

Microchemistry. When the acetone extract of *P. notata* was recrystal-lized from GE (1 volume of glycerin+3 volumes of glacial acetic acid), it yielded two kinds of colourless crystals along with pale yellow prisms of usnic acid. They formed aggregates of straight needles and clusters of curved fine needles. The aggregates of straight needles were identical with crystals obtained from pure samples of 4-O-methylhypoprotocetraric acid (Pl. II, fig. 1), while the needle clusters are those yielded by notatic acid (Pl. II, fig. 2).

Thin layer chromatographic tests on the depsidones (I) and (II) were conducted on glass slides  $(5\times10\,\mathrm{cm})$  coated with Merk silica gel G. The chromatograms could be developed in a mixed hexane, ether, formic acid solvent (10:8:1) (Kurokawa 1967) and developed by spraying with 10%

The structure of these new depsidones follow from a combination of spectroscopic properties, chemical interconversions and synthetic experiments which will be reported elsewhere.

sulphuric acid followed by subsequent warming. Here 4-O-methylhypoprotocetraric acid (I) gave a spot at Rf. 0.42 (bluish-green turning violet) and notatic acid (II) a spot at Rf. 0.37 (green turning purple-brown).

Alternatively these compounds could be developed in a mixed benzene, dioxane, glacial acetic acid solvent (90:25:4) (Huneck 1968) and developed by spraying with 10% alcoholic ferric chloride solution. Here (I) gave a blue-violet spot at Rf. 0.60 and (II) a purple spot at Rf. 0.53.

### Literature cited

Culberson, Chicita F. 1966. The structure of a new depsidone from the lichen *Parmelia livida*. Phytochemistry 5: 815-818. Huneck, S. 1968. Lichen substances in L. Reinhold & Y. Liwschitz: Progress in Phytochemistry 1: 223-346. Kurokawa, S. 1967. On the occurrence of diffractaic, physodalic, and psoromic acids in *Parmeliae*. Bull. Nat. Sci. Mus. Tokyo 10: 369-376.

## Explanation of Plates I-II

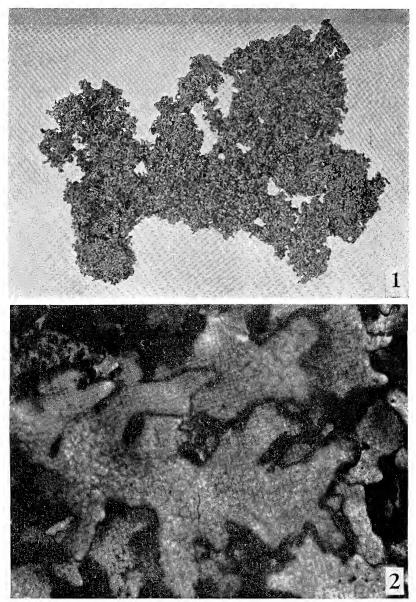
Plate I. Fig. 1. Holotype of *Parmelia notata* Kurokawa (ca.  $\times$  3/5). Fig. 2. Lobes of *Parmelia notata* Kurokawa, showing effigurate maculae on the upper surface ( $\times$ 6).

Plate II. Fig. 1. 4-O-Methylhypoprotocetraric acid recrystallized in GE. Fig. 2. Notatic acid recrystallized in GE.

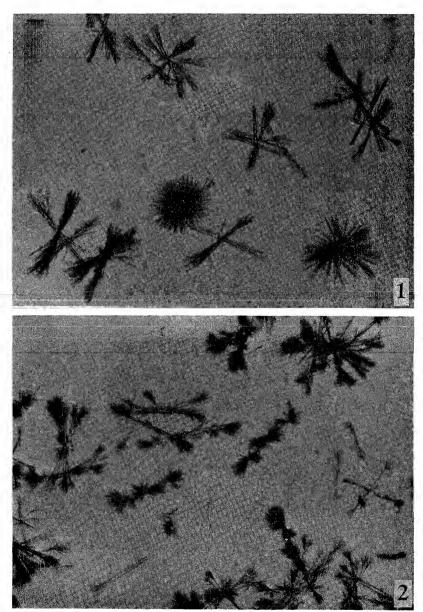
オーストラリア産の Xanthoparmelia の一新種 Parmelia notata (Pl. I, Fig. 1) から新しい 2 つのデプシドンが得られ,両者の構造が明らかになったので報告した。 2 つのデプシドンは 4-O-メチルヒポプロトセトラール酸 (I) とノタート酸 (II) で,どちらも GE 液から再結晶される (Pl. II, Figs. 1, 2)。一方,P. notata はこれらのデブシドンを含むことと, 地衣体表面に顕著な斑紋のあること (Pl. I, Fig. 2) で特徴づけられ,オーストラリア東南部に広く分布し,西オーストラリアとタスマニアでも採集されている。

Oアケボノスミレの長葉形(橋本 保・芹沢俊介) Tamotsu Hashimoto & Shunsuke Serizawa: A long-leaved form of Viola rossii.

高尾山から奥武蔵にかけての低い山地には、 アケボノスミレの葉が細長い一形があ



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KUROKAWA, ELIX, WATSON & SARGENT: Parmelia notata